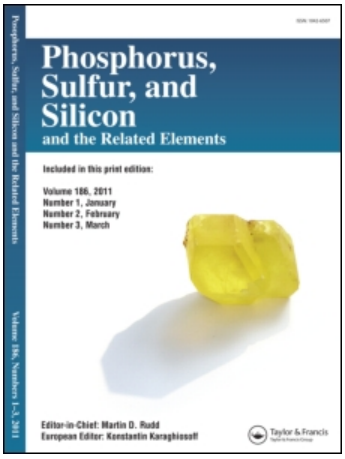

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Trimethylsilyl and Trimethylstannyl Esters of Trithiophosphonic Acid, Starting Compounds for the Synthesis of S-P-Heterocycles

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Trimethylsilyl and Trimethylstannyl Esters of Trithiophosphonic Acid, Starting Compounds for the Synthesis of S-P-Heterocycles

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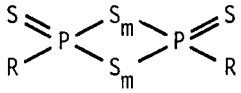
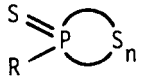
The silyl and stannyl esters of trithiophosphonic acids $RP(S)(SEMe_3)_2$ (E = Si, Sn; R = Me, t-Bu) are formed in high yield from the corresponding phosphanes $RP(EMe_3)_2$ by the addition of three sulfur atoms (3/8 S_8). The stannyl esters can also be obtained from the silyl esters and $SnMe_3Cl$ or by reacting dithiophosphonic acid anhydrides $[RP(S)S]_2$ with $(SnMe_3)_2S$. As a result of the preformed P-S-bonds and the reactivity of the S-E-bond towards Cl_2, Br_2 as well as chlorosulfanes S_xCl_2, the esters represent ideal starting compounds for the synthesis of sulfur-phosphorus-heterocycles of general formulas A and B.



$[RP(S)S_m]_2$, m = 2-4

A



$RP(S)S_n$, n = 5-7

B

The tetrathiadiphosphorinanes $[RP(S)S_2]_2$, the products of the reaction with the halogens, are also formed in excellent yield when the silyl esters are treated with dimethylsulfoxide.

Conformational changes of the heterocycles have been studied by ^{31}P and ^{1}H D-NMR spectroscopy. In consequence of the small difference between the P-S- and S-S-bond length the results obtained provide insight into the dynamic processes of the corresponding sulfur rings S_{n+1} and S_{2m+2}, respectively, which cannot be studied by direct methods.